Superconductivity and Cobalt Oxidation State in $Na_xCoO_2 \cdot 4xH_2O$ ($x \sim 1/3$)

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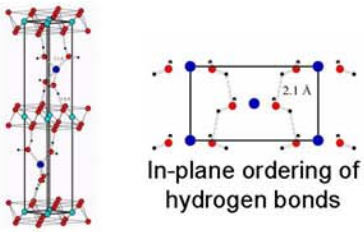
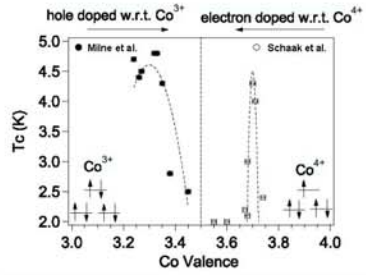
Motivation: To investigate the effects of synthetic chemistry, temperature and pressure on the oxidation state of cobalt in superconducting $Na_xCoO_2 \cdot 4xD_2O$ ($x \sim 1/3$).

$Na_{1/3}CoO_2 \cdot {}^4/_3H_2O$ Crystal Structure

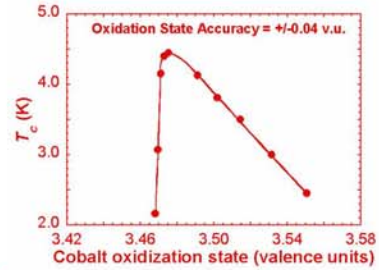


J. D. Jorgensen *et al.*
Phys. Rev. B **68**, 214517 (2003).

Previously Reported Superconducting Phase Diagrams

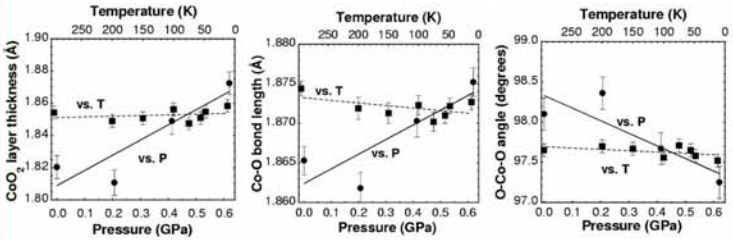


Superconducting Phase Diagram (This Work)

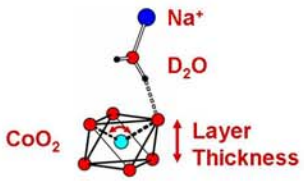


Temperature and Pressure Effects on the Crystal Structure of $Na_{1/3}CoO_2 \cdot {}^4/_3D_2O$

- Thermal expansion and compressibility were monitored using neutron powder diffraction. As expected, anisotropic thermal expansion occurs ($\Delta c/c > \Delta a/a$) with increasing T; however, the CoO_2 layer thickness increases with increasing P.



- CoO_2 layer thickness is controlled by the Co–O bond length and the O–Co–O angle.

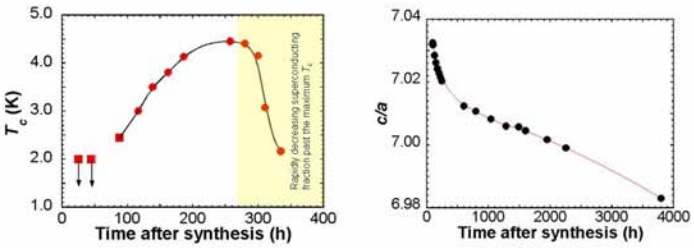


- This increase in layer thickness is attributed to P-induced strengthening of the H-bonds between the CoO_2 layers and the D_2O molecules. The strengthened H-bonds requires a charge redistribution that weakens the Co–O bonds, thus changing the electronic structure of the material (decreased Co valence).

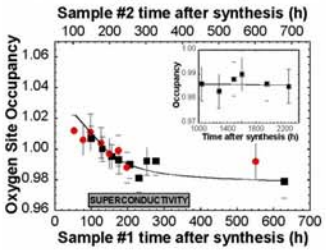
J. D. Jorgensen *et al.*, *Phys. Rev. B* **72**, 224515 (2005).

Determination of the Superconducting Phase Diagram Using a Single Sample

- T_c and the c/a ratio of metastable $Na_{1/3}CoO_2 \cdot {}^4/_3D_2O$ (made in one step using a Br_2/D_2O solution) vary as a function of time after synthesis.



- These changes are due to oxygen vacancy formation within the CoO_2 planes.



- At high Co oxidation states, $Na_{1/3}CoO_2 \cdot {}^4/_3D_2O$ is metastable. Oxygen vacancies form in the CoO_2 planes, lowering Co^{n+}. T_c increases as Co^{n+} decreases, reaching a maximum near $n \approx +3.5$, followed by a rapid decrease attributed to charge ordering.

Impact: This work illustrates how neutron powder diffraction is combined with other techniques to probe important structural variables such as ordering, defect concentrations and charge states that impact a material's physical properties.

Future Work: This project is part of an ongoing program on layered superconductors. Future work will focus on searching for superconductivity in new layered compounds, including structural analogs to $Na_xCoO_2 \cdot 4xH_2O$, compounds with the K_2NiF_4 structure, and layered nitrides, phosphides, and borides.

P. W. Barnes, M. Avdeev, J. D. Jorgensen, D. G. Hinks, H. Claus, and S. Short. Phys. Rev. B 72, 134515 (2005).

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